Synthesis of diacetals from aldehydes and ketones with pentaerythritol catalysed by the $ZrO_2/S_2O_8^{2-}$ solid superacid

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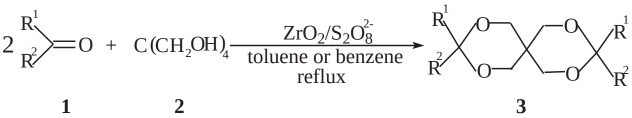
A manipulatively simple and rapid procedure for the synthesis of diacetals from 2,2-bis(hydroxymethyl)-1, 3-propanediol with aldehydes and ketones in refluxing benzene or toluene using the $ZrO_2/S_2O_8^{2-}$ solid superacid as catalyst in 80–98% yields has been described.

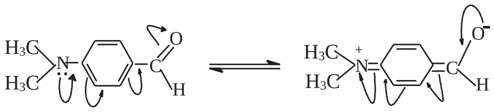
Keywords: synthesis, diacetals, pentaerythritol, catalyst, solid superacid

Pentaerythritol diacetals are useful in many fields. They can be applied as plasticisers and vulcanisers of various of polymeric materials, as raw materials for production of valuable resins and lacquers, as physiologically active substances[1] and as defoamers in washing solutions containing anionic surfactants.[2] Diacetals also can be used as containing a potential protective group for aldehydes and ketones and are important derivatives of carbonyl compounds since most of them are crystalline substances and have sharp melting points. The preparation of pentaerythriol diacetals has been described under acidic conditions. There are protic acids, such as sulfuric acid,[3,4] hydrochloric acid[5] and *p*-toluenesulfonic acid,[6-8] which have been employed as catalysts and there are Lewis acids, such as zinc chloride[9] and anhydrous cupric sulfate,[10] which have also been reported as catalysts to this kind of reaction. However, these catalysts have not been entirely satisfactory, due to drawbacks such as the occurrence of secondary reactions (oxidation, dehydration and etherification), the corrosion of equipment, the contamination of the environment, long reaction times, non-recoverability of the catalyst, *etc*. Consequently there is a demand for environmentally friendly acid catalysts for the synthesis of pentaerythritol diacetals under mild conditions. Cation exchanger KU-2[1] and 12-tungstophosphoric acid[11] have been used as catalysts for the condensation of 2,2-bis(hydroxymethyl)-1,3-propanediol with aldehydes and ketones. More recently, microwave irradiation,[12] montmorillonite,[13] expansive graphite[14] and anhydrous ferrous sulfate[15] were applied to accelerate the reaction.

Solid superacids are known to catalyse a variety of organic reactions.[16-18] Recently, we have developed efficient and convenient procedures for the preparation of aromatic oximes and mandelates catalysed by the ZrO_2/SO_4^{2-}solid superacid.[16, 19] As a part of ongoing work on solid superacid catalysts, we now describe a direct condensation of aldehydes and ketones with 2,2-bis (hydroxymethyl)-1,3-propanediol catalysed by $ZrO_2/S_2O_8^{2-}$ [20] in excellent yield (Scheme 1).



Scheme 1



Scheme 2

As summarised in Table 1, some aldehydes and ketones were heated with 2,2-bis-(hydroxymethyl)-1,3-propanediol in the presence of $ZrO_2/S_2O_8^{2-}$ in refluxing benzene or toluene. Use of toluene involves a potentially less hazardous procedure, the corresponding diacetals were obtained in good to excellent yield. The reaction proceeds cleanly and the work-up is simple, involving only filtration of the catalyst and removal of solvent to obtain the product.[21]

We found that the reaction rate is markedly dependent on temperature. The reaction proceeded much more slowly in refluxing benzene than in toluene. For example, complete conversion of 3-chlorobenzaldehyde (**1k**) into the corresponding diacetal needed 0.5h in refluxing toluene, but 1.0h in refluxing benzene under catalysis of $ZrO_2/S_2O_8^{2-}$. We also observed that ketones show less reactivity than aldehydes in this reaction, for example, pentaerythritol diacetal (**3c**) was obtained in quantitative yield (94%) in refluxing benzene in 1.5h whereas acetophenone diacetal (**3t**) was formed in 80% yield in refluxing toluene for 8h in the presence of $ZrO_2/ S_2O_8^{2-}$. It is worth noting that when 4- or 2-hydroxybenzaldehyde was treated with 2, 2-bis(hydroxymethyl)-1,3-propanediol in the presence of $ZrO_2/S_2O_8^{2-}$, we obtained nothing, even though the reaction took longer (>8h) under refluxing in toluene. We propose that the hydroxyl group complexes with the Zr ion, so the activity of the catalyst is decreased. However, it is highly probable that the methoxy group of vanillic aldehyde (**1m**) prevents the complexation of the hydroxyl group with the Zr ion in this case as the vanillic aldehyde (**1m**), which also contains an hydroxyl group, reacts to give the product in 85% yield. 4-(Dimethylamino)benzaldehyde also does not react rapidly; the reason may be that the strong donor dimethylamino group reduces the reactivity. The resonance involving the of quinoid structure would decrease the reactivity of the aldehyde group (Scheme 2).

The catalysts are easily regenerated by washing with ethanol followed by drying at 120°C for 4 h. The catalyst could be reused 5 times for the synthesis of pentaerythritol diacetal (**3k**) without significant loss of activity.

In conclusion, we have provided an efficient and convenient method for the synthesis of 2,2-bis(hydroxymethyl)-1, 3-propanediol diacetals catalysed by $ZrO_2/S_2O_8^{2-}$. The reaction works well without removing the formed water and the present procedure appears to be efficient for aldehydes, aliphatic ketones and monoaryl ketones but not for diaryl ketones. This method possesses the advantages of the operational simplicity, short reaction times, use of inexpensive materials, absence of corrosion and pollution, high yields and reusable catalysts.

Experimental

Melting points are uncorrected.^1H NMR spectra were determined on a Varian VXR-300S (300 MHz) spectrometer using $CDCl_3$ as solvent and tetramethylsilane (TMS) as internal reference. IR spectra were determined on an FTS-175C spectrometer. All the liquid parent materials were fresh stilled. The products were also characterised by comparison of their melting points with literature values. The catalyst $ZrO_2/S_2O_8^{2-}$ solid superacid was prepared as follows. $Zr(OH)_4$ was

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Table 1 Preparation of diacetals catalysed by $ZrO_2/S_2O_8^{2-}$

Entry	Substrate	Solvent	Time /h	Yield[a,b]/%	Mp/°C	
					Found[c]	Reported
1	$CH_3CH_2CH_2CHO$ (**1a**)	Toluene	0.5	96	43–44	43–44[11]
2	$CH_3(CH_2)_5CHO$ (**1b**)	Toluene	0.5	94	63–64	62–63[14]
3	C_6H_5CHO (**1c**)	Toluene	0.5	96	155–156	155–156[12]
		Benzene	1.5	94		
4	4-MeC_6H_4CHO (**1d**)	Toluene	1.0	95	211–212	211–233[13]
5	4-$MeOC_6H_4CHO$ (**1e**)	Toluene	1.5	95	176–177	180–182[13]
6	3,4-$(OCH_2O)C_6H_3CHO$ (**1f**)	Toluene	0.5	96	188–189	188[13]
7	4-$NO_2C_6H_4CHO$ (**1g**)	Toluene	0.25	90	227–228	227–228[13]
		Benzene	1.0	92		
8	3-$NO_2C_6H_4CHO$ (**1h**)	Toluene	0.5	92	185–186	185[13]
9	2-$NO_2C_6H_4CHO$ (**1i**)	Toluene	1.0	95	164–165	163–164[12]
		Benzene	1.5	94		
10	4-ClC_6H_4CHO (**1j**)	Toluene	1.0	96	198–199	197–198[12]
		Benzene	1.0	92		
11	3-ClC_6H_4CHO (**1k**)	Toluene	0.5	98	121–122	121–122[12]
		Benzene	1.0	97		
12	2,4-$Cl_2C_6H_3CHO$(**1l**)	Toluene	1.0	97	186–187	
13	4-HO-3-$MeOC_6H_3CHO$ (**1m**)	Toluene	2.5	85	167–170	170–171[13]
14	4-$Me_2NC_6H_4CHO$ (**1n**)	Toluene	8.0	82	221–223	223[13]
15	$C_6H_5CH{=}CHCHO$ (**1o**)	Toluene	0.5	94	190–192	195[13]
16	α-Furaldehyde (**1p**)	Toluene	1.5	90	159–160	158–159[12]
17	$CH_3CO(CH_2)_5CH_3$ (**1q**)	Toluene	3.0	90	43–45	44–45[13]
18	Cyclopentanone (**1r**)	Toluene	5.0	91	115–117	
19	Cyclohexanone (**1s**)	Toluene	4.0	94	112–113	112–113[11]
20	$C_6H_5COCH_3$ (**1t**)	Toluene	8.0	80	147–148	147–148[13]
21	$(C_6H_5CH_2)_2CO$ (**1u**)	Toluene	5.0	94	165–167	166–167[13]
22	$(C_6H_5)_2CO$ (**1v**)	Toluene	8.0			

[a]Yield refer to isolated pure products. [b]Products are characterised by ^1H NMR and IR.[21] [c]Products are characterised by their physical constants.

infused in an aqueous $(NH_4)_2S_2O_8$ solution (1 mol/l) for 4 hours, then filtered off, dried at 110°C for 2 hours, crushed over 150 mesh, dried and calcined in a furnace at 600°C for 4 hours and finally stored in a desiccator until used.

General procedure for preparation of diacetals: A mixture of the carbonyl compound (**1,** 2.00 mmol), 2,2-bis(hydroxymethyl)-1, 3-propanediol (**2,** 1.25 mmol) and $ZrO_2/S_2O_8^{2-}$ (100 mg) in benzene or toluene (10 ml) was stirred at refluxing temperature for 0.5–8 h (the use of benzene (an established aranogen) involves a potentially more hazardous procedure) (Table 1). The progress of the reaction was monitored with TLC. After completion of the reaction, the mixture was cooled, the catalyst was filtered off and washed by CH_2Cl_2 (5 ml×2). Evaporation of the solvent under reduced pressure afforded the crude product. The crude product was purified by column chromatography on silica gel with light petroleum–diethyl ether as eluent or recrystallised to give diacetals **3** yield 80–98% (Table 1). Selected spectral data of some of the products are given below:

3a: ν_{max}/cm^{-1} 2960, 2932, 2872, 1160, 1114, 1078, 994, 724; δ_H 0.90(6 H, t, *J*=6.1Hz, CH_3), 1.20–1.70(8 H, m, CH_2), 3.25–3.70(6 H, m, H_{eq}, H_{ax}), 4.40(2H, t, *J*=4.4Hz, CH), 4.65 (2 H, d, *J*=11.4Hz, H_{eq})

3b: ν_{max}/cm^{-1} 2956, 2928, 2855, 1470, 1385, 1161, 1112, 1030, 942; δ_H 0.89(6 H, t, CH_3), 1.27–1.62(20 H, m, CH_2), 3.20–4.52(10 H, m, OCH_2, CH)

3c: ν_{max}/cm^{-1} 3066, 3035, 2920, 2857, 1607, 1497, 1205, 1162, 1116, 1087, 1023, 749; δ_H 3.50–3.95(6 H, m, H_{eq}, H_{ax}), 4.80(2 H, d, *J*=11.4Hz, H_{eq}), 5.42(2 H, s, ArCH), 7.20–7.58(10 H, m, ArH)

3d: ν_{max}/cm^{-1} 2910, 2862, 1600, 1460, 1390, 1050, 805; δ_H 2.35 (6 H, s, CH_3), 3.64(2 H, d, *J*=11.7Hz, H_{ax}), 3.79–3.85(4 H, m, H_{eq}), 4.58(2 H, d, *J*=11.7Hz, H_{ax}), 5.42(2 H, s, ArCH), 7.18(4 H, d, *J*=8.0Hz, 3', 5'- ArH), 7.37(4 H, d, *J*=8.0Hz, 2',6'-ArH)

3k: ν_{max}/cm^{-1} 2968, 2856, 1577, 1479, 1381, 1074, 966, 702; δ_H 3.66(2 H, d, *J*=11.4 Hz, H_{ax}), 3.84(4 H, d, *J*=11.4Hz, H_{eq}), 4.83 (2 H, d, *J*=11.4 Hz, H_{ax}), 5.43(2 H, s, ArCH), 7.31–7.38(6 H, m, 4',5', 6'-ArH), 7.50 [2 H, s, 2'-ArH]

3l: ν_{max}/cm^{-1} 2977, 2934, 2867, 1600, 1472, 1387, 1211, 1083, 955, 822, 759; δ_H 3.71(2H, d, *J*=11.6 Hz, H_{ax}), 3.84–3.92 (4 H, m, H_{eq}), 4.88(2 H, d, *J*=11.2 Hz, H_{ax}), 5.78(2 H, s, ArCH), 7.31(2 H, d, *J*=8.4Hz, 6'-ArH), 7.41(2 H, d, *J*=8.4 Hz, 5'-ArH), 7.65(2 H, d, *J*=8.4 Hz, 3'-ArH)

3m: ν_{max}/cm^{-1} 3407, 2858, 1604, 1522, 1383, 1163, 1075, 1027, 864, 780; δ_H 3.65(2 H, d, *J*=11.5Hz, H_{ax}), 3.80–3.86 (4 H, m, H_{eq}), 4.87(2 H, d, *J*=11.5Hz, H_{ax}), 3.92(6 H, s, OCH_3), 5.40(2 H, s, ArCH), 5.67(2 H, br s, OH), 6.91(2 H, d, *J*=8.2Hz, 5'-ArH), 6.97(2 H, d, *J*=8.2Hz, 6'-ArH), 7.03(2 H, s, 2'-ArH)

3p: ν_{max}/cm^{-1} 3124, 2987, 2972, 2868, 1606, 1505, 1678, 1117, 1085, 1028, 795, 742; δ_H 3.50–3.95(6 H, m, H_{eq}, H_{ax}), 4.80(2 H, d, *J*=11.4Hz, H_{eq}), 5.55(2 H, s, CH), 6.30–6.53(4 H, m, β-H), 7.40(2 H, t, α-H)

3q: ν_{max}/cm^{-1} 2970, 2865, 1470, 1380, 1160, 1075; δ_H 0.88[6 H, t, $(CH_2)_5\mathbf{CH_3}$], 1.28(16 H, m, CH_2), 1.35(6 H, s, CH_3), 1.66(4 H, t, *J*=7.9Hz, CH_2), 3.71–3.88(8 H, m, CH_2O)

3r: ν_{max}/cm^{-1} 2933, 2855, 1450, 1255, 1162, 1100, 1044, 922, 844; δ_H 1.53–1.58(8 H, m, α-H), 1.73–1.75(8 H, m, β-H), 3.75–3.87(8H, s, CH_2O)

3t: ν_{max}/cm^{-1} 2980, 2900, 1470, 1380, 1250, 1175, 890, 704; δ_H 1.50(6 H, s, CH_3), 3.15 (2 H, dd, *J*=11.1Hz, *J*=2.4Hz, 2×H_{eq}), 3.25 (2 H, d, *J*=11.1Hz, 2×H_{ax}), 3.63(2 H, d, *J*=11.7Hz, 2×H_{ax}), 4.47(2 H, dd, *J*=11.7Hz, *J*=2.4Hz, 2×H_{eq}), 7.31–7.42(10 H, m, Ar H)

3u: ν_{max}/cm^{-1} 2990, 2855, 1600, 1480, 1075, 750, 702; δ_H 2.88 (8 H, s, $ArCH_2$), 3.59(8 H, s, CH_2O), 7.14–7.32(20 H, m, Ar H)

We wish to thank the Natural Science Fund (29872011), the Educational Ministry of China, the Educational Department of Hebei Province (990104) and the Science and Technology Commission of Hebei Province for support of this work.

Received 23 September 2003; accepted 22 January 2004
Paper 03/2121

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